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THE EXACT EXPANSION OF THE ELECTRONIC ENERGY
OF ONE-ELECTRON DIATOMIC MOLECULES IN
POWERS OF THE INTERNUCLEAR SEPARATION

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ABSTRACT   11118

The exact expansion of the electronic energy of the ground state
of one-electron diatomic molecules through the fourth order in powers
of the internuclear separation is derived by using the methods intro-
duced by Hylleraas (1931). It is thereby shown that the straightforward
perturbation treatment of the electronic energy of molecules based on
the united atom as given by Bingel (1959) leads to incorrect results
for the third order coefficient. The exact fourth order coefficient is
checked by using the Hellmann-Feynman theorem to relate the expansion
to the well known formula for the electrostatic potential due to a
hydrogen-like atom.

AUTHOR

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THE EXACT EXPANSION OF THE ELECTRONIC ENERGY OF ONE-ELECTRON DIATOMIC MOLECULES IN POWERS OF THE INTERNUCLEAR SEPARATION

Introduction

The total energy of a diatomic molecule AB with internuclear separation R may be written

$$E(R) = W(R) + Z_a Z_b / R \qquad (1)$$

where W is the electronic energy and Z_a, Z_b are the atomic numbers of the nuclei. Since the electronic energy is finite for all values of R it is natural to assume that it is analytic and may be expanded about $R = 0$ in powers of R :

$$W(R) = W_0 + RW_1 + \tfrac{1}{2}R^2 W_2 + \tfrac{1}{6} R^3 W_3 + \tfrac{1}{24} R^4 W_4 + \cdots \qquad . \qquad (2)$$

The leading term $W_0 = W(0)$ is the energy of the united atom with atomic number $Z = Z_a + Z_b$, and the other coefficients are similarly properties of the united atom. The coefficients may be obtained in two different ways:

(a) By means of the formulae of standard perturbation theory based on the united atom and with the perturbation potential

$$V = \sum_{i=1}^{N} \left(\frac{Z}{r_i} - \frac{Z_a}{r_{ai}} - \frac{Z_b}{r_{bi}} \right)$$

where r_{ai} , r_{bi} and r_i are the distances of the ith electron from nucleus A , nucleus B and the centre of nuclear charge. Bingel (1959)[1] has proposed such a treatment and has expanded the first order perturbation energy through terms in R^3 .

(b) By regarding (2) as a Taylor series expansion with

$$W_n = (\partial^n W / \partial R^n)_{R=0} \qquad (3)$$

and evaluating the derivatives of the integral for the electronic energy,

$$W = \int \psi H \psi \, d\tau \quad , \tag{4}$$

with respect to R at $R = 0$. This has been carried out by Steiner (1961)[2] through the fourth derivative by extending the technique used by Brown (1958)[3].

Both methods can be used in general for any molecule and the straightforward application of either of them leads to the same expressions for the coefficients W_n. However, while there is no doubt about the correctness of the value of W_1, which vanishes, or of the general expression for the second-order derivative $W_2 = W''(0)$, it is clear from Steiner's work that the expression for the third coefficient W_3 cannot be correct. Furthermore, as Steiner showed, these methods give the absurd result that the fourth coefficient appears to be infinite.

The object of this paper is to obtain the coefficients in equation (2) for the only case in which they can be evaluated exactly, namely that of a one-electron diatomic molecule. These values can then be used as a critique for attempts to rectify the methods mentioned above.

Electronic Energy for One-Electron Molecules

Before presenting the detailed analysis of the Schrödinger equation for this case we shall collect together all the information about the electronic energy $W(R, Z_a, Z_b)$ which can be obtained by simple methods.

The simplest feature is the symmetry with respect to the interchange of nuclei A and B. Since the scalar distance R is invariant to such an interchange,

$$W(R, Z_b, Z_a) = W(R, Z_a, Z_b) \quad . \tag{5}$$

A second general property, peculiar to one-electron molecules, is that W is homogeneous and of degree two in Z_a, Z_b and $1/R$. This follows from the Schrödinger equation for the system by scaling the

electronic coordinates by λ, which leads to

$$W(R/\lambda, \lambda Z_a, \lambda Z_b) = \lambda^2 W(R, Z_a, Z_b) \quad , \tag{6}$$

which proves the property. In view of the symmetry and homogeneity relations we could write W in the form

$$W(R, Z_a, Z_b) = Z^2 w(RZ, R^2 Q^2) \tag{7}$$

where $Q = Z_a - Z_b$.

Several limiting values of W are known.

(a) United atom, $R = 0$: $W = -\tfrac{1}{2} Z^2$.

(b) Separated atoms, $R = \infty$: $W = -\tfrac{1}{2} Z_a^2 \ (Z_a > Z_b)$.

(c) Atom A , $Z_b = 0$: $W = -\tfrac{1}{2} Z_a^2$; similarly for B.

Also three limiting values of derivatives are known and can be used to check the expansion.

(a) The force between the nuclei due to the electronic motion vanishes at the united atom, so that

$$(\partial W / \partial R)_{R=0} = W_1 = 0 \quad . \tag{8}$$

The proof is simple and is based on the inversion symmetry of the united atom charge density[1,2].

(b) By the Hellmann-Feynman Theorem

$$(\partial W / \partial Z_b)_{Z_b = 0} = \phi_a(R) \tag{9}$$

where $\phi_a(R)$ is the electrostatic potential due to atom A at distance R from the nucleus and is given by

$$\phi_a(R) = -\int \frac{\rho_a(r)}{|r - R|} d\tau \tag{10}$$

where $\rho_a(r)$ is the electron density of atom A .

(c) The coefficient $W_2 = W''(0)$ is well established and is related to the electron density $\rho_{UA}(0)$ and field gradient at the nucleus. For S states of the united atom the relation is[1,2]

$$W_2 = (\partial^2 W/\partial R^2)_{R=0} = \frac{4\pi}{3} \frac{Z_a Z_b}{Z} \rho_{UA}(0) \quad . \tag{11}$$

A simple physical argument for the vanishing of W_1 and the value of W_2 given by equation (11) is as follows. The electric field at a point distance r from the centre of an atom in an S-state is $\mathcal{E} = Q(r)/r^2$ where $Q(r)$ is the total charge within a sphere of radius r . When r is very small $Q(r) = -(4\pi/3)\rho_{UA}(0)r^3$ and therefore $\mathcal{E}(r) = -(4\pi/3)\rho_{UA}(0)r$. The force on nucleus A a short distance R_a from the united atom centre is therefore $F_a = Z_a \mathcal{E}(R_a)$, assuming that the charge distribution is unaltered to this order of approximation. The equilibrium position of the united atom centre is such that $F_a = F_b$ or $Z_a R_a = Z_b R_b$, and hence the force $F = F_a = F_b$ between A and B at distance $R = R_a + R_b$ apart, due to the electrons, is

$$F = -\frac{4\pi}{3} \rho_{UA}(0) \frac{Z_a Z_b}{Z} R \quad . \tag{12}$$

Since $F = -\partial W/\partial R$ it follows immediately that $W_1 = -F(0) = 0$ and $W_2 = -F'(0)$ is given by (11).

Separation of the Schrödinger Equation

The Schrödinger equation for the system, which is

$$\left(\tfrac{1}{2}\nabla^2 + \frac{Z_a}{r_a} + \frac{Z_b}{r_b} + W \right) \psi = 0 \quad \text{(atomic units)} , \tag{13}$$

may be separated by introducing confocal elliptic coordinates ξ , η , ϕ , the first two being defined by

$$\xi = (r_a + r_b)/R \quad , \qquad \eta = (r_a - r_b)/R \quad , \tag{14}$$

and ϕ being the azimuthal angle. For $\sum$ states, which are axially symmetric, the wave function may be written in the form

$$\psi = H(\eta)X(\xi) \qquad (15)$$

where H and X satisfy the "inner" and "outer" equations

$$\frac{d}{d\eta}\left[(1 - \eta^2)\frac{dH}{d\eta}\right] + (-RQ\eta + p^2\eta^2 - C)H = 0 \qquad (-1 \le \eta \le 1) , \quad (16)$$

$$\frac{d}{d\xi}\left[(\xi^2 - 1)\frac{dX}{d\xi}\right] + \left(RZ\xi - p^2\xi^2 + C\right)X = 0 \qquad (1 \le \xi \le \infty) , \quad (17)$$

where

$$p^2 = -\tfrac{1}{2}R^2 W \qquad (18)$$

and C is the separation constant. Note that the outer equation (17) depends only on the sum of the atomic numbers $Z = Z_a + Z_b$ and the inner equation only on their difference $Q = Z_a - Z_b$.

The procedure we shall follow to obtain the expansion of W in powers of R is that introduced by Hylleraas[4] in solving the equations to any accuracy. The method is to expand the function $H(\eta)$ in terms of Legendre polynomials and from the resulting determinant of elimination to obtain the expansion of C in powers of p and RQ . By treating the outer equation for $X(\xi)$ in a similar fashion and equating the two expressions for C it is possible to obtain the coefficients in the expansion of W in powers of R .

Expansion of Inner Equation

Consider a solution of equation (16) in the form[4,5]

$$H(\eta) = \sum_{\ell=0}^{\infty} h_\ell P_\ell(\eta) \qquad (19)$$

where $P_\ell(\eta)$ is the ℓth Legendre polynomial, satisfying the differential equation, similar to (16),

$$\frac{d}{d\eta}\left[(1 - \eta^2)\frac{dP_\ell}{d\eta}\right] + \ell(\ell + 1)P_\ell = 0 \quad . \tag{20}$$

By substituting (19) into (16) and using the recurrence relation for P_ℓ twice to eliminate terms in η and η^2 we get

$$h_\ell\left\{C + \ell(\ell + 1) - p^2\left[\frac{2\ell(\ell + 1) - 1}{(2\ell + 3)(2\ell - 1)}\right]\right\} + h_{\ell+1}q\left(\frac{\ell + 1}{2\ell + 3}\right) + h_{\ell-1}q\left(\frac{\ell}{2\ell - 1}\right)$$

$$- h_{\ell+2}p^2\frac{(\ell + 2)(\ell + 1)}{(2\ell + 5)(2\ell + 3)} - h_{\ell-2}p^2\frac{\ell(\ell - 1)}{(2\ell - 1)(2\ell - 3)} = 0 \quad , \quad (\ell = 0,1,2,\cdots) \tag{21}$$

where $q = RQ$. This is a five-term recurrence relation for the coefficients h_ℓ, which leads to the determinantal equation

$$\begin{vmatrix} C - p^2/3 & q/3 & -2p^2/15 & 0 & \cdot \\ q & C + 2 - 3p^2/5 & 2q/5 & -6p^2/35 & \cdot \\ -2p^2/3 & 2q/3 & C + 6 - 11p^2/21 & 3q/7 & \cdot \\ 0 & -2p^2/5 & 3q/5 & C + 12 - 23p^2/45 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0 \ . \tag{22}$$

We are interested in an expression for C when R is small, which is valid for the ground state. For the lowest state $C = 0$ when $R = 0$, and since p and q are of order R, to the first approximation

$$\begin{vmatrix} C - p^2/3 & q/3 \\ q & 2 \end{vmatrix} = 0 \quad \text{or} \quad C = p^2/3 + q^2/6 \quad . \tag{23}$$

This suffices to determine the coefficients through W_3 in the expansion of W. To find the term of order R^4 in C we put $k = q/p$ (order unity) and

$$C = \frac{p^2}{3} (1 + \tfrac{1}{2}k^2) + p^4 f + O(p^6) \qquad (24)$$

where f is a function of k , of order unity, to be determined.
By substituting (24) into (22), retaining all relevant terms and re-moving a factor of p^2 we get

$$\begin{vmatrix} k^2/6 + p^2 f & k/3 & -2p/15 & 0 \\ k & 2 - p^2(4/15 - k^2/6) & 2kp/5 & 0 \\ -2p/3 & 2kp/3 & 6 & 3kp/7 \\ 0 & 0 & 3kp/5 & 12 \end{vmatrix} = 0 \qquad (25)$$

By expanding and retaining terms up to p^2 this gives eventually

$$f = (2 + 5k^2 - 11k^4/8)/135 \qquad ,$$

which can be substituted into (24) to give

$$C = \frac{p^2}{3} (1 + \tfrac{1}{2}k^2) + \frac{2p^4}{135} (1 - \frac{k^2}{4})(1 + \frac{11k^2}{4}) + O(R^6) \qquad . \quad (26)$$

Expansion of Outer Equation

To solve the outer equation systematically we consider a solution of the form proposed by Jaffé[5], namely

$$X(\xi) = e^{-p\xi} (1 + \xi)^{s/2p-1} \sum_{n=o}^{\infty} x_n \left(\frac{\xi - 1}{\xi + 1} \right)^n \qquad (27)$$

where s = RZ . This is a modification of Hylleraas's original expansion, in terms of Laguerre functions of argument $(\xi - 1)$, which is mathe-matically more satisfactory. By substituting (27) into (17) we get the three-term recurrence relation

$$x_{n-1}(s/2p - n)^2 + x_n\left[C + s/2p + s - (p + 1)^2 + 2n(s/2p - 1 - n - 2p)\right]$$

$$+ x_{n+1}(n + 1)^2 = 0 \quad , \quad (n = 0,1,2,\cdots) \quad . \tag{28}$$

The determinantal equation which arises from the elimination of the coefficients is

$$\begin{vmatrix} C - a & 1 & 0 & 0 & \cdot \\ b^2 & C - a - 2(1 + 2p + b) & 2^2 & 0 & \cdot \\ 0 & (1 + b)^2 & C - a - 4(2 + 2p + b) & 3^2 & \cdot \\ 0 & 0 & (2 + b)^2 & C - q - 6(3 + 2p + b) & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0 \quad , \tag{29}$$

where

$$a = (1 + p)^2 - s - s/2p \quad , \quad b = 1 - s/2p \quad . \tag{30}$$

When $R = 0$ we have $p = s = 0$ and since $W(0) = -\tfrac{1}{2}z^2$ it follows that $a = b = 0$. The first approximation for the ground state value of C is therefore

$$C \cong a \quad , \tag{31}$$

from which it can be shown that the coefficient of the linear term, W_1, vanishes, in accordance with equation (8). It follows that a and b are of order R^2, and therefore (31) is valid through terms in R^3. The next approximation is to solve the equation

$$
\begin{vmatrix}
C - a & 1 & 0 & 0 & \cdot \\
b^2 & -2 & 2^2 & 0 & \cdot \\
0 & 1 & -2.2^2 & 3^2 & \cdot \\
0 & 0 & 2^2 & -2.3^2 & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot
\end{vmatrix} = 0 \quad . \tag{32}
$$

This involves a bordered determinant which may be expanded to give

$$
C - a = b^2 g
$$

where g is a continued fraction which reduces to

$$
g = \frac{1}{-2-} \; \frac{1}{-2-} \; \frac{1}{-2-} \; \cdots \quad .
$$

It follows that $g = 1/(-2-g)$ with the solution $g = -1$, and therefore

$$
C = a - b^2 \quad . \tag{33}
$$

By substituting for a and b from (30) we get

$$
C = 2p - s + p^2 + (1 - s/2p)s/2p + O(R^5) \quad , \tag{34}
$$

where the order of magnitude of the neglected terms follows from the fact that $C - a$ and b^2 are of order R^4.

Energy Expansion

By equating expressions (26) and (34) for C we get an implicit equation for p as a function of $s = RZ$ and $q = kp = RQ$. Let the expansion of p in powers of R be

$$
p = \tfrac{1}{2}s \left[1 + \alpha R^2 + \beta R^3 + \gamma R^4 + O(R^5) \right] \quad , \tag{35}
$$

so that

$$W = -\tfrac{1}{2}Z^2 \left[1 + 2\alpha R^2 + 2\beta R^3 + (2\gamma + \alpha^2)R^4 \right] + O(R^5) \quad .$$

(36)

To find the coefficients α, β, γ we substitute (35) into the equation for C , expand, and equate the coefficients of powers of R to zero. This leads straightforwardly to the result

$$W = -\tfrac{1}{2}Z^2 + \tfrac{2}{3} Z_a Z_b (RZ)^2 - \tfrac{2}{3} Z_a Z_b (RZ)^3 + \tfrac{2}{5} Z_a Z_b (1 - 64 Z_a Z_b / 27 Z^2)(RZ)^4 + \cdots$$

(37)

According to the general theory the second coefficient W_2 is given by equation (11). Since $\rho_{UA}(0) = Z^3/\pi$ for the ground state (1s) of a one electron atom, (11) gives

$$W_2 = \tfrac{4}{3} Z_a Z_b Z^2 \quad ,$$

(38)

which agrees with equation (37).

To get some check on W_3 and W_4 we can use the Hellmann-Feynman result (9). The potential due to a hydrogen-like atom, defined by (10), is given by

$$\phi_a(R) = (Z_a + 1/R) e^{-2Z_a R} - 1/R \quad .$$

(39)

Expanding in powers of R we get

$$(\partial W/\partial Z_b)_{Z_b = 0} = -Z_a \left[1 - \tfrac{2}{3}(RZ_a)^2 + \tfrac{2}{3}(RZ_a)^3 - \tfrac{2}{5}(RZ_a)^4 + \cdots \right] \quad .$$

(40)

An identical expression is obtained by differentiating (37) with respect to Z_b , thus partly checking the expressions for W_3 and W_4 .

For the hydrogen molecule-ion, $Z_a = Z_b = 1$, (37) becomes

$$W = -2 + \tfrac{8}{3} R^2 - \tfrac{16}{3} R^3 + \tfrac{352}{135} R^4 + \cdots \quad .$$

(41)

Comparison with General Treatment

The general expression derived by Bingel[1] using first-order perturbation theory based on the united atom is

$$W = -\tfrac{1}{2}Z^2 + \frac{2}{3} Z_a Z_b (RZ)^2 - \frac{2}{3} Z_a Z_b \left(\frac{Z_a^2 + Z_b^2}{Z^2} \right) (RZ)^3 + \cdots \quad .$$

(42)

Bingel's treatment therefore gives the wrong form for W_3, which for homopolar molecules, and in particular H_2^+, is too small by a factor of 2[*]. A preliminary investigation of the discrepancy[2] shows that it is connected with failure to take into account the non-analytic behaviour of the molecular wave function near the nuclei as $R \rightarrow 0$.

Acknowledgements

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[*] Note, however, that since it is correct to the first-order in Z_b, it leads to the correct coefficient in $(\partial W / \partial Z_b)_0$.

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